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## Densification and Sintering of a Microwave-Plasma-Synthesized Iron Nanopowder

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### ABSTRACT

Powder compacts made from microwave-plasma-synthesized iron (Fe) nanopowder (Materials Modification Inc., Fairfax, VA) were sintered under hydrogen ( $H_2$ ). Results showed that without the application of pressure, the powder could not be sintered to full density. In subsequent experiments, the powder was consolidated to final densities near 80% of the theoretical full density, using plasma pressure compaction ( $P^2C$ ). To provide an explanation for the difficulty in attaining full densification, the precursor powder and compacted pellet characteristics were examined by several methods. These included residual porosity by mercury pycnometry, surface area measurement by Brunauer, Emmett, and Teller (BET) analysis, and structural change by x-ray diffraction (XRD) and scanning electron microscopy (SEM). It was observed that the nanosized primary particles were aggregated into micrometer-sized dendritic structures, with the appearance of tumbleweeds. The observed limitations in the densification and associated porous microstructures of the pressureless-sintered and  $P^2C$ -densified compacts were rationalized in terms of the behavior of the dendritic aggregate structures rather than that of the nanosized primary particles.

### INTRODUCTION

A widely accepted method for preparation of full-density nanograined material entails comminution of micrometer-sized powder to nanoscale by high-energy ball milling followed by sinter forging [1]. However, the fabrication of large, fully dense nanostructured metal bodies remains an unrealized goal. A promising alternative to comminution is the direct synthesis of the nanopowder by microwave plasma synthesis (MPS). Iron (Fe) bodies of 95% theoretical density (TD) have been reported by moderate-pressure consolidation of precursor powder by plasma pressure compaction ( $P^2C$ ) at 850 °C [2]. The mean particle size of the precursor was measured to be ~500 nm, the grain size of the final part was on the order of 10  $\mu m$ . The primary advantage of  $P^2C$ , also known as plasma activated sintering (PAS), is the ability to apply large DC or AC currents through a powder sample, causing the formation of a plasma arc, whereby the interior temperatures rise rapidly. The plasma causes the evolution of impurities, and a simultaneous application of moderate pressure densifies the sample material. Detailed descriptions of PAS can be found in several references [3,4].

A representative lot of MPS Fe nanopowder was obtained from Materials Modification Inc., Fairfax, VA. Fe nanopowder green compacts were pressureless sintered in a hydrogen ( $H_2$ ) atmosphere with the objective of relating the precursor characteristics and properties to its sintering behavior. Results showed that without pressure, there was difficulty in attaining full density samples. Subsequently, several attempts were made to further densify the Fe using  $P^2C$ .

The nanoprecursor was examined by nitrogen sorption, x-ray diffraction analysis (XRD), and field emission scanning electron microscopy (FESEM). Density of the sintered compacts was determined by mercury pycnometry, and the microstructure was examined by scanning electron microscopy (SEM). The pressureless sintering and P<sup>2</sup>C results, in context of the precursor characteristics and with implications for the production of bulk samples, are discussed.

## EXPERIMENTAL PROCEDURE

The bulk tap density was determined by weighing the as-received Fe powder and dividing by the filled container volume. FESEM was performed on a Hitachi S4700 F-SEM (Nissei Sangyo America, Gaithersburg, MD). Nitrogen gas adsorption analysis was performed on a Micromeritics ASAP 2010 Accelerated Surface Area and Porosimetry System (Micromeritics, Norcross, GA). Two samples, outgassed at 200 °C under vacuum, were subjected to six-point Brunauer, Emmet, and Teller (BET) surface area analysis. Another full adsorption isotherm was collected as well. A Philips APD1700 Automated Powder Diffractometer System (Philips Analytical, Natick, MA) was used for the line broadening XRD analysis, scanning the most intense Fe peaks; the net peak height under each peak was at least 10,000 counts. The instrumental broadening was determined by scanning characteristic peaks of LaB<sub>6</sub> near the Fe peaks. After subtracting the instrumental broadening contribution, Scherrer's equation [5] was used to determine the particle size.

Several 1-g green compacts were pressed uniaxially at 55 MPa. Density was determined based on measurements of the compact thickness and diameter. Pressureless sintering was performed at 300, 500, 700, or 900 °C for 30 min under a 10 l/min flow of dry H<sub>2</sub>. The sintered pellets were halved. One half was used to determine pellet density using mercury pycnometry in a Micromeritics Autopore IV Model 9510 Mercury Porosimeter Analyzer (Micromeritics, Norcross, GA). The other half was mounted and polished for SEM examination; the polished surfaces were etched with 2% Nital to reveal the microstructure.

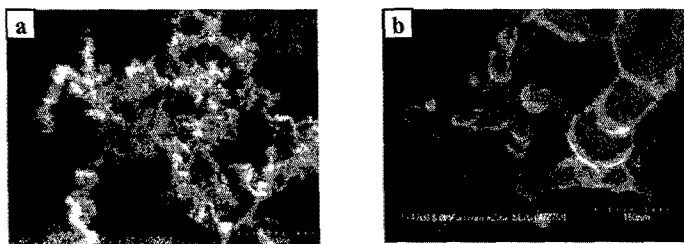
Similarly sized green compacts were loaded in a 1.27-cm inner diameter graphite die assembly. A two-color optical pyrometer was focused on the center of the die to measure the external temperature as the power level through the sample was raised. In each P<sup>2</sup>C run, DC current was ramped at 100 A/min such that the target temperature was reached in a few minutes. At the same time, a 127-MPa constant pressure was applied to the samples. Higher pressures caused the dies to crack or shatter. When a predetermined time elapsed at the selected temperature, the current was ramped down to 0 A, and the pressure was released. After cooling, the P<sup>2</sup>C samples were extracted and analyzed in the same manner as those obtained from pressureless sintering.

## RESULTS AND DISCUSSION

### Powder Characteristics

FESEM images, depicted in Figure 1, show a particle size of 50-80 nm. There are no isolated Fe particles; instead, grains appear to be fused to each other, forming chainlike tentacles, with an average size of 0.3-1 μm. Note that the particle-particle necks are a strong evidence of sintering

during MPS. BET plots were linear, with a BET  $c$  constant of 42, implying that the powders were free of fine pores and that an effective diameter may be calculated from a hard-sphere model. Using the BET surface area of 13,866 or 15,079  $\text{m}^2\text{kg}^{-1}$ , a hard-sphere model, and a 7,870  $\text{kgm}^{-3}$  density for Fe, the equivalent diameter range was found to be 50 or 56 nm. This is consistent with the FESEM results. XRD line-broadening analysis of each of the four Fe peaks yielded a smaller average crystallite size of about  $20 \pm 3$  nm.

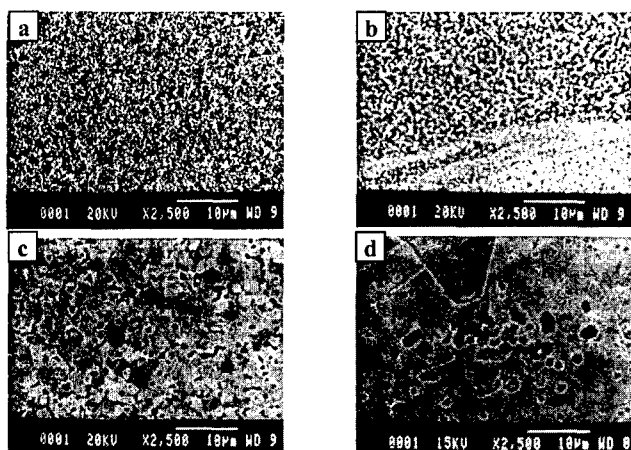


**Figure 1.** FESEM micrographs of the Fe powder are shown with the aggregate structure in (a) and the individual particles in (b).

### **Pressureless Sintering Results**

The bulk density of the powder was 0.13  $\text{gcm}^{-3}$ , or 1.6 %TD of Fe. The powder proved to be pyrophoric, sometimes combusting during die filling or compaction. Green density of the compacts was approximately 40 %TD. Regardless of sintering temperature, the consolidated pellets delaminated, though the macroscopic appearance improved with increasing temperatures. At the lower two temperatures, the pellets were black and rough. At the higher two temperatures, the pellets had only one or two lateral delaminations, but were blistered with a silvery exterior surface. Interior surfaces were also shiny.

As shown in Figure 2, there is little or no coarsening of the individual Fe particles at 300 °C. The dendritic aggregate structure of the Fe clusters is still present. In some isolated areas, necking and the onset of coarsening were observed. At 500 °C, further coarsening and banding takes place. Once 700 °C is exceeded, any remaining evidence of the initial dendritic structure and morphology is lost. Submicrometer voids, or closed pores, remain at the triple points between the 3-4- $\mu\text{m}$ -sized grains. Finally, heterogeneous grain growth at 900 °C of the recrystallized Fe grains dominates the microstructure. (There are a few polishing scratches in some of the soft grains.) Submicrometer voids also coalesce into 5-10- $\mu\text{m}$  void agglomerates or void bands. Summarized in Table I, the effect of temperature is limited on the density; full- or near-full density could not be achieved. Note the extreme grain growth with temperature. Despite a lack of densification, as shown in the table, the grain size of the consolidated Fe pellets dramatically increases with temperature. Assuming an Arrhenius behavior for atom diffusion and associated grain growth, a least squares fit to the data yields an activation energy of  $62 \pm 6$  kJ/mol, which is only one-fourth of that for the self-diffusion of Fe [6].



**Figure 2.** Backscattered electron micrographs of the pressureless sintered samples are shown with 300 °C in (a), 500 °C in (b), 700 °C in (c), and 900 °C in (d).

**Table I.** Pressureless Sintering Results

Temperature (°C)	Density (gcm <sup>-3</sup> )	Density (%TD)	Average Grain Size (µm)
300	3.52	44.7	0.05
500	4.52	57.4	1.
700	5.87	74.6	5.
900	5.87	74.6	50.

## **P<sup>2</sup>C Results**

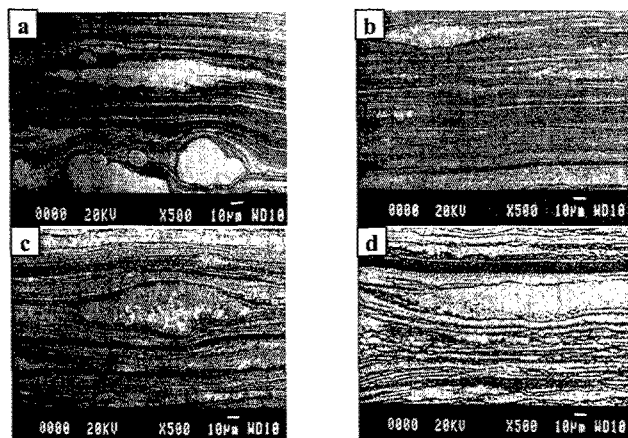
Unlike the pressureless sintered samples, the P<sup>2</sup>C samples were not delaminated. Results of the experiments are listed in Table II. As apparent, the variations of time or temperature have a relatively minor effect on the overall density of the samples. Under moderate pressure, the initially isotropic agglomerates form highly oriented (transverse to the compaction axis), filamentary structures of alternating dense and porous strata (see Figure 3). At 600 °C, the interior of these filaments consists of dendritic aggregates that sintered into a coarsened, yet porous spongy structure. Note the formation of anomalously more dense regions. A comparison of the two samples at 600 °C shows that at low temperatures, the effect of time is negligible on the microstructure. At higher temperatures, especially at 800 and 1000 °C, these filamentary layers grow denser. The interior of these bands consists of 2-3-µm grains, interspersed with isolated submicrometer-sized porosity. Particles in less dense regions coarsen as well, resulting in a random distribution of isolated fine, nanosized droplets.

It has been postulated that increased interfacial and surface-free energies in nanosized particles would enhance diffusion and thereby facilitate sintering at lower temperatures [7]. The well

bonded particles within the dendritic arms seem to support this argument. However, no enhanced low-temperature, solid-state sintering or concomitant densification occurs during pressureless sintering. Gain in density is seen only above the secondary recrystallization temperature of Fe (450 °C). Additionally, the observed coarsening and densification behavior are consistent with a thermally activated process and follow the behavior of larger, conventionally sized powders [8]. The use of the P<sup>2</sup>C provides a little gain in densification, but with an added extrinsic, current-induced structural asymmetry that is imparted to the sintered body.

**Table II.** P<sup>2</sup>C Results

Temperature (°C)	Time (min)	Density (gcm <sup>-3</sup> )	Density (%TD)
600	1	6.20	78.8
600	15	6.25	79.4
800	5	5.90	75.0
1000	1	6.06	77.0



**Figure 3.** SEM images of the P<sup>2</sup>C samples are shown with 600 °C, 1 min in (a), 600 °C, 15 min in (b), 800 °C, 5 min in (c), and 1000 °C, 1 min in (d).

The sintering properties of this MPS powder vis-à-vis a conventional powder can be understood in terms of the dendritic structures shown in Figure 1. Both pressureless sintered and P<sup>2</sup>C samples' structural heterogeneity (i.e., banding) is a result of the dendritic agglomerates. That is, although initially enhanced sintering takes place between adjacent particles, the open structure of extended dendritic arms prevents any further possible coalescence and collapse of the partly necked and coarsened structure. It is suspected that because of shorter cycling times, there is less grain growth during P<sup>2</sup>C, however, the pressure brought to bear on the green body as to break up the agglomerates is insufficient to fully densify the P<sup>2</sup>C samples.

## CONCLUSIONS

A MPS Fe nanopowder, consisting of 0.3-1  $\mu\text{m}$  dendritic agglomerates of 50-60 nm spheroidal particles, was sintered using  $\text{P}^2\text{C}$ . The pressureless sintering behavior of this powder indicated that the dendritic structure of the nanopowder hindered solid-state sintering into a fully dense body. No enhanced sintering below the recrystallization temperature was observed. The initial size and morphology of the Fe, however, were completely lost at 500  $^{\circ}\text{C}$ . Using  $\text{P}^2\text{C}$  (high DC current and low pressure), the structure was stratified with suppressed grain growth, but without an increase in density. The implications were twofold: on one hand, if the nanostructure was to be retained, sintering had to be conducted below this temperature. On the other hand, direct sintering of nanopowders to dense bodies required more careful control of the MPS process to avoid formation of low-density agglomerates. While it may be possible to introduce further processing steps, for now, conventional pressing and pressureless sintering of such agglomerates to full-density bodies is extremely difficult.

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